

# Van der Waals interactions in DFT made easy by Wannier functions

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(Dated: February 1, 2008)

## Abstract

Ubiquitous Van der Waals interactions between atoms and molecules are important for many molecular and solid structures. These systems are often studied from first principles using the Density Functional Theory (DFT). However, the commonly used DFT functionals fail to capture the essence of Van der Waals effects. Many attempts to correct for this problem have been proposed, which are not completely satisfactory because they are either very complex and computationally expensive or have a basic semiempirical character. We here describe a novel approach, based on the use of the Maximally-Localized Wannier functions, that appears to be promising, being simple, efficient, accurate, and transferable (charge polarization effects are naturally included). The results of test applications are presented.

DFT represents a well-established tool to study the structural and electronic properties of molecules and condensed matter systems from first principles, and to elucidate complex processes such as surface adsorptions, catalytic reactions, and diffusive motions. Although current density functionals are able to describe well several systems, at much lower computational cost compared to other first principles methods, they fail to do so[1] for the description of long-range dispersion effects, generally denoted as Van der Waals (VdW) interactions, particularly the leading  $R^{-6}$  term originated from correlated instantaneous dipole fluctuations; the cases where DFT (using, for instance the Local Density Approximation, LDA, or the PBE[2] functionals) provides reasonable estimates for the interaction energy of weakly bound system are actually due to favorable errors or cancellations and should therefore be considered accidental.

In order to overcome this severe deficiency of DFT, two basic strategies have been adopted: on one hand, new density functionals or/and relatively complex schemes have been proposed that in principle allow for a correct treatment of the VdW interactions [1, 3, 4, 5, 6, 7, 8, 9], on the other hand several semiempirical approaches[10, 11] have been developed where an approximately derived  $R^{-6}$  term, multiplied by a suitable short-range damping function, is explicitly introduced. Although both these approaches have been somehow successful, neither of them appears to be entirely satisfactory: in fact, the former is generally quite complex and computationally very demanding, compared to a standard DFT calculation, while the latter, based on interatomic  $C_6$  coefficients (actually dependent on the molecular environment of the atoms involved) and empirical fits, turns out to be far from generally applicable because it neglects changes in the atomic polarizabilities (which, in general, are not additive) and should be tailored to the specific system considered. Therefore the development of a practical efficient scheme to include VdW interactions in DFT remains a great theoretical challenge.

In this paper we propose a novel method which allows the efficient calculation of the VdW interaction between nonoverlapping fragments, using as input only the ground state electron density and the Kohn-Sham (KS) orbitals computed in a conventional DFT approach.

Crucial to our analysis is the use of the Maximally-Localized Wannier function (MLWF) formalism[12], that allows the total electronic density to be partitioned, in a chemically transparent and unambiguous way, into individual fragment contributions. The MLWFs represent a generalization, for systems characterized by periodic boundary conditions, of

the Boys' localized orbitals[13] that are commonly used in quantum chemistry; they allow for an intuitive interpretation of the bonding properties of condensed-matter systems[12] and are at the center of the modern theory of polarization[14]. The MLWFs,  $\{w_n(\mathbf{r})\}$ , are generated by performing a unitary transformation in the subspace of the occupied KS orbitals, obtained by a standard DFT calculation, so as to minimize the total spread:

$$S = \sum_n S_n = \sum_n \left( \langle w_n | r^2 | w_n \rangle - \langle w_n | \mathbf{r} | w_n \rangle^2 \right) . \quad (1)$$

Besides its spread,  $S_n$ , each MLWF is characterized also by its Wannier-function center (WFC); for instance, if periodic boundary conditions are used with a cubic supercell of side  $L$ , the coordinate  $x_n$  of the  $n$ -th WFC is defined[12] as

$$x_n = -\frac{L}{2\pi} \text{Im} \ln \langle w_n | e^{-i\frac{2\pi}{L}x} | w_n \rangle , \quad (2)$$

with similar definitions for  $y_n$  and  $z_n$ . If spin degeneracy is exploited, every MLWF corresponds to 2 paired electrons. Starting from these MLWFs the leading  $R^{-6}$  VdW correction term can be evaluated using different possible recipes; one of them is described and applied in the following. We make the reasonable (at least for insulating systems) assumption[15] of exponential localization of the MLWFs in real space, so that each of them is supposed to be an hydrogen-like, normalized, function, centered around its WFC position,  $r_n$ , with a spread  $S_n$ :

$$w_n(|\mathbf{r} - \mathbf{r}_n|) = \frac{3^{3/4}}{\sqrt{\pi} S_n^{3/2}} e^{-\frac{\sqrt{3}}{S_n} |\mathbf{r} - \mathbf{r}_n|} . \quad (3)$$

Then the binding energy of a system composed of two fragments is given by  $E_b = E_0 + E_{\text{VdW}}$ , where  $E_0$  is the binding energy obtained from a standard DFT calculation, while the VdW correction is assumed to have the form:

$$E_{\text{VdW}} = - \sum_{n,l} f_{nl}(r_{nl}) \frac{C_{6nl}}{r_{nl}^6} , \quad (4)$$

where  $r_{nl}$  is the distance of the  $n$ -th WFC, of the first fragment, from the  $l$ -th WFC of the second one, the sum is over all the MLFWs of the two fragments, and the  $C_{6nl}$  coefficients can be calculated directly from the basic information (center positions and spreads) given by the MLFWs. In fact, using for instance the expression proposed by Andersson *et al.*

(see Eq. (10) of ref.[4]) that describes the long-range interaction between two separated fragments of matter:

$$C_{6nl} = \frac{3}{32\pi^{3/2}} \int_{|\mathbf{r}| \leq r_c} d\mathbf{r} \int_{|\mathbf{r}'| \leq r'_c} d\mathbf{r}' \frac{\sqrt{\rho_n(r)\rho_l(r')}}{\sqrt{\rho_n(r)} + \sqrt{\rho_l(r')}} = \frac{3}{32\pi^{3/2}} \int_{|\mathbf{r}| \leq r_c} d\mathbf{r} \int_{|\mathbf{r}'| \leq r'_c} d\mathbf{r}' \frac{w_n(r)w_l(r')}{w_n(r) + w_l(r')}, \quad (5)$$

where  $\rho_n(r) = w_n^2(r)$  is the electronic density corresponding to the  $n$ -th MLWF,  $C_{6nl}$  is given in a.u., and the  $r_c, r'_c$  cutoffs have been introduced[3, 4] to properly take into account both the limit of separated fragments and of distant disturbances in an electron gas: by equating the length scale for density change to the electron gas screening length one obtains:

$$\frac{6\rho_n(r_c)}{|\vec{\nabla}\rho_n(r_c)|} = \frac{v_F[\rho_n(r_c)]}{\omega_p[\rho_n(r_c)]}, \quad (6)$$

where  $v_F = (3\pi^2\rho_n(r))^{1/3}/m$  is the local Fermi velocity, and  $\omega_p = (4\pi e^2\rho_n(r)/m)^{1/2}$  is the local plasma frequency. By using the analytic form (see Eq. (3)) of the MLWFs, it is straightforward to obtain the cutoff expressed in terms of the MLWF spread:

$$r_c = S_n\sqrt{3}(0.769 + 1/2\ln(S_n)) , \quad (7)$$

and to evaluate very efficiently the multidimensional integral of Eq. (5). For instance, in the test case of 2, distant H atoms, using the well known (unperturbed) analytic H atom wavefunction, the above formula gives  $C_6 = 6.41$  a.u. to be compared to the reference literature value of 6.50 a.u.

In Eq. (5), if the electronic density corresponding to every MLWF is multiplied by 2, the  $C_{6nl}$  coefficients increase by a  $\sqrt{2}$  factor; therefore it appears reasonable to assume that, when each MLWF describes 2 paired electrons (spin degeneracy),  $C_{6nl}$  has to be multiplied by  $\sqrt{2}$ . This is also supported by the fact that, in the Slater-Kirkwood approximation for estimating the  $C_6$  coefficients, the effective number of electrons is smaller than the number of valence electrons, and it is  $1.42 \simeq \sqrt{2}$  in the case of the He atom[16], whose DFT ground state is just given by 2 paired electrons in the lowest-energy KS orbital.

In Eq. (4)  $f_{nl}(r)$  is a damping function which serves to cutoff the unreasonable behavior of the asymptotic VdW correction at small fragment separations. For it we have chosen a form[11, 17] with parameters directly related to the MLWF spreads:

$$f_{nl}(r) = \frac{1}{1 + \exp(-a(r/R_s - 1))} , \quad (8)$$

where[17]  $a \simeq 20$  (the results are almost independent on the particular value of this parameter), and  $R_s = R_{\text{VdW}} + R'_{\text{VdW}}$  is the sum of the VdW radii of the MLWFs, which, following Grimme *et al.*[17], are determined as the radii of the 0.01 electron density contour; using Eq. (3) one easily obtains that:

$$R_{\text{VdW}} = (1.475 - 0.866 \ln(S_n)) S_n . \quad (9)$$

The damping function effectively reduces the VdW correction to zero typically below 2 Å; at intermediate distances a minimum in the VdW potential exists that usually lies slightly below the sum of the corresponding VdW radii,  $R_s$ . Note that the above recipe resembles that proposed in ref. [18], where the long-range electron-electron interaction is separated by the short-range one, using a single parameter describing the physical dimensions of a valence electron pair.

The  $E_0$  binding energy can be obtained from a standard DFT calculation (we have used the CPMD[19] and  $\nu$ -ESPRESSO[20] ab initio packages), using the Generalized Gradient Approximation (GGA) in the revPBE flavor[21]. This choice[8, 17] is motivated by the fact that revPBE is fitted to the exact Hartree-Fock exchange, so that the VdW binding, a correlation effect, only comes from the VdW correction term, as described above, without any double-counting effect (for instance, LDA, or other GGA functionals, such as PBE, predict substantial binding in rare gas dimers, due to a severe overestimate of the long-range part of the exchange contribution[8]). The evaluation of the VdW correction as a post-standard DFT perturbation, using the revPBE electronic density distribution, represents an approximation because, in principle a full self-consistent calculations should be performed; however recent investigations[22] on different systems have shown that the effects due to the lack of self-consistency are negligible (this is reasonable because one does not expect that the rather weak and diffuse VdW interaction substantially changes the electronic charge distribution).

The VdW correction scheme described above can be refined by considering the effects due to the anisotropy of the MLWFs, and distinguishing between contributions along (or orthogonal to) the fragment-fragment direction (details will be published elsewhere[23]). Moreover,

also higher-order term VdW corrections, involving the  $C_8$ ,  $C_{10}$ ,... coefficients, could be easily included. Clearly, in the present method, the evaluation of the VdW corrections to the interfragment forces is trivial, thus allowing an easy implementation in standard geometry optimization calculations or Molecular Dynamics simulations. Remarkably, the whole procedure of generating the MLWFs and evaluating the VdW corrections represents a negligible additional computational cost, compared to that of a standard DFT calculation.

We have applied the new method to selected dimers among typical VdW-bonded systems:  $\text{Ar}_2$ ,  $\text{N}_2\text{-N}_2$  (“T-shaped”),  $\text{CH}_4\text{-CH}_4$ ,  $\text{C}_6\text{H}_6\text{-C}_6\text{H}_6$  (“sandwich-shaped”),  $\text{C}_6\text{H}_6\text{-Ar}$ ,  $\text{CO}_2\text{-CO}_2$ , and also a mixed (H-bonded/VdW-bonded) complex,  $\text{C}_6\text{H}_6\text{-H}_2\text{O}$ .

In the Tables I-III we report our computed binding energy (a positive value indicates unbound complexes), equilibrium characteristic interdimer distance, and fragment-fragment effective  $C_6$  coefficient, which is defined as  $\sum_{n,l} C_{6nl}$  (in fact, neglecting the differences in the spreads of the MLWFs and in the interfragment distances between the WFCs,  $E_{\text{VdW}} \sim -f \left( \sum_{n,l} C_{6nl} \right) / R^6$ , where  $R$  is the interdimer distance). These values are compared to the most reliable (to our knowledge) reference literature corresponding data, which are often spread over a relatively large range (comparison with literature  $C_6$  coefficients should be taken as purely indicative because of different assumed definition). As can be seen, the general performance of the method is quite satisfactory; in fact, the improvement achieved by including the VdW correction, with respect to the pure revPBE results, is dramatic, even in the case of a mixed complex, such as  $\text{C}_6\text{H}_6\text{-H}_2\text{O}$ , where some fraction of the binding energy is already given by the standard DFT calculation. In Fig. 1 we show the effect of the inclusion of the VdW correction on the behavior of the binding energy of the  $\text{Ar}_2$  dimer, plotted as a function of the Ar-Ar distance, and compared to the reference equilibrium value; in Ar the 8 valence electrons of each atom are described by 4 MLWFs (spin degeneracy is exploited), whose WFCs are tetrahedrally located around the Ar ion.

In the case of the equilibrium characteristic distances, the more substantial deviation from the reference results can easily be explained by the fact that the potential energy curves for weakly-bonded systems are typically very shallow. Inspection of Table I shows that anisotropy effects do not much affect the binding energy estimates, but for the case of the “sandwich-shaped” benzene dimer, where anisotropy correction leads to a value much closer to the reference data: this behavior comes as no surprise, since the planar geometry of the two fragments clearly induces strong anisotropy in the computed MLWFs. In Table I, by

considering the MLWF anisotropy, the binding energies are always decreased and lower than the reference values; this behavior is probably due to the neglect of higher-order contributions to the VdW correction, such as the  $-C_8/R^8$  term (dipole-quadrupole interaction), which should be included to have a very accurate estimate of the binding energy[24].

We have also applied our technique to the case of graphite, where the optimal interlayer distance, found to be 8.69 Å with the standard DFT-revPBE approach, becomes 6.33 Å by including VdW effects, that is much closer to the experimental value (6.70 Å).

In conclusion, we have presented and applied in test cases a technique suitable to describe VdW effects in the framework of standard DFT calculations. The technique is based on the generation of the MLWFs and naturally describes changes in the electronic density distributions of the fragments due to the environment, for instance related to charge polarization effects: in fact these changes are easily described in terms of changes in the location of the centers and in the spreads of the MLWFs. The results of the method, which is simple to be implemented and not expensive computationally, are quite satisfactory and promising, also considering that a large area for future improvements exists: in fact, different, more sophisticated schemes to utilize the MLWFs could be developed and/or improved reference DFT functionals, with respect to revPBE, could be adopted.

We thank F. Ancilotto, M. Boero, F. Toigo, and F. Valencia for useful discussions. We acknowledge funding from Padua University project n. CPDA033545 and PRIN 2004 (“NANOTRIBOLOGIA” project), and allocation of computer resources from INFN “Progetto Calcolo Parallelo”.

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TABLE I: Binding energy, in meV, computed using the standard DFT-revPBE calculation,  $E_0$  and including the VdW correction,  $E_0 + E_{\text{VdW}}$ , compared to available literature data; in parenthesis values, computed taking anisotropy effects into account, are reported.

system	$E_0$	$E_0 + E_{\text{VdW}}$	ref
Ar-Ar	-1.7	-11.9 (-9.5)	-12.3
N <sub>2</sub> -N <sub>2</sub>	-2.9	-11.1 (-10.8)	-13.3
CH <sub>4</sub> -CH <sub>4</sub>	-2.1	-11.7 (-9.9)	-23↔-14
C <sub>6</sub> H <sub>6</sub> -C <sub>6</sub> H <sub>6</sub>	+7.1	-252.7 (-144.1)	-142↔-61
C <sub>6</sub> H <sub>6</sub> -Ar	-2.4	-65.7 (-53.5)	-65
CO <sub>2</sub> -CO <sub>2</sub>	-16.2	-54.0 (-47.9)	-69↔-59
C <sub>6</sub> H <sub>6</sub> -H <sub>2</sub> O	-40.4	-131.2 (-121.6)	-169↔-137

TABLE II: Equilibrium characteristic interdimer distance, in Å, computed using the standard DFT-revPBE calculation,  $R_0$  and including the VdW correction,  $R_{\text{VdW}}$ , compared to available literature data; in parenthesis values, computed taking anisotropy effects into account, are reported.

system	$R_0$	$R_{\text{VdW}}$	ref
Ar-Ar	4.67	4.03 (4.07)	3.76
N <sub>2</sub> -N <sub>2</sub>	5.05	4.37 (4.37)	4.03
CH <sub>4</sub> -CH <sub>4</sub>	4.70	4.23 (4.25)	3.60↔4.27
C <sub>6</sub> H <sub>6</sub> -C <sub>6</sub> H <sub>6</sub>	—	3.45 (3.45)	3.80↔3.90
C <sub>6</sub> H <sub>6</sub> -Ar	4.79	3.57 (3.57)	3.41
CO <sub>2</sub> -CO <sub>2</sub>	3.86	3.49 (3.49)	3.60
C <sub>6</sub> H <sub>6</sub> -H <sub>2</sub> O	4.23	3.17 (3.17)	3.40↔3.50

TABLE III: Fragment-fragment effective  $C_6$  coefficient (see text for the definition), in a.u., computed using the standard DFT-revPBE with the VdW correction, compared to available literature data; in parenthesis values, computed taking anisotropy effects into account, are reported.

system	$C_6$	ref
Ar-Ar	92.5 (74.7)	64.3↔65.5
N <sub>2</sub> -N <sub>2</sub>	90.3 (95.6)	73.4
CH <sub>4</sub> -CH <sub>4</sub>	103.0 (101.0)	118.0↔130.0
C <sub>6</sub> H <sub>6</sub> -C <sub>6</sub> H <sub>6</sub>	2930.0 (2460.0)	1723.0
C <sub>6</sub> H <sub>6</sub> -Ar	490.0 (448.0)	330.1
CO <sub>2</sub> -CO <sub>2</sub>	187.0 (172.0)	—
C <sub>6</sub> H <sub>6</sub> -H <sub>2</sub> O	323.0 (299.0)	208.5↔277.4

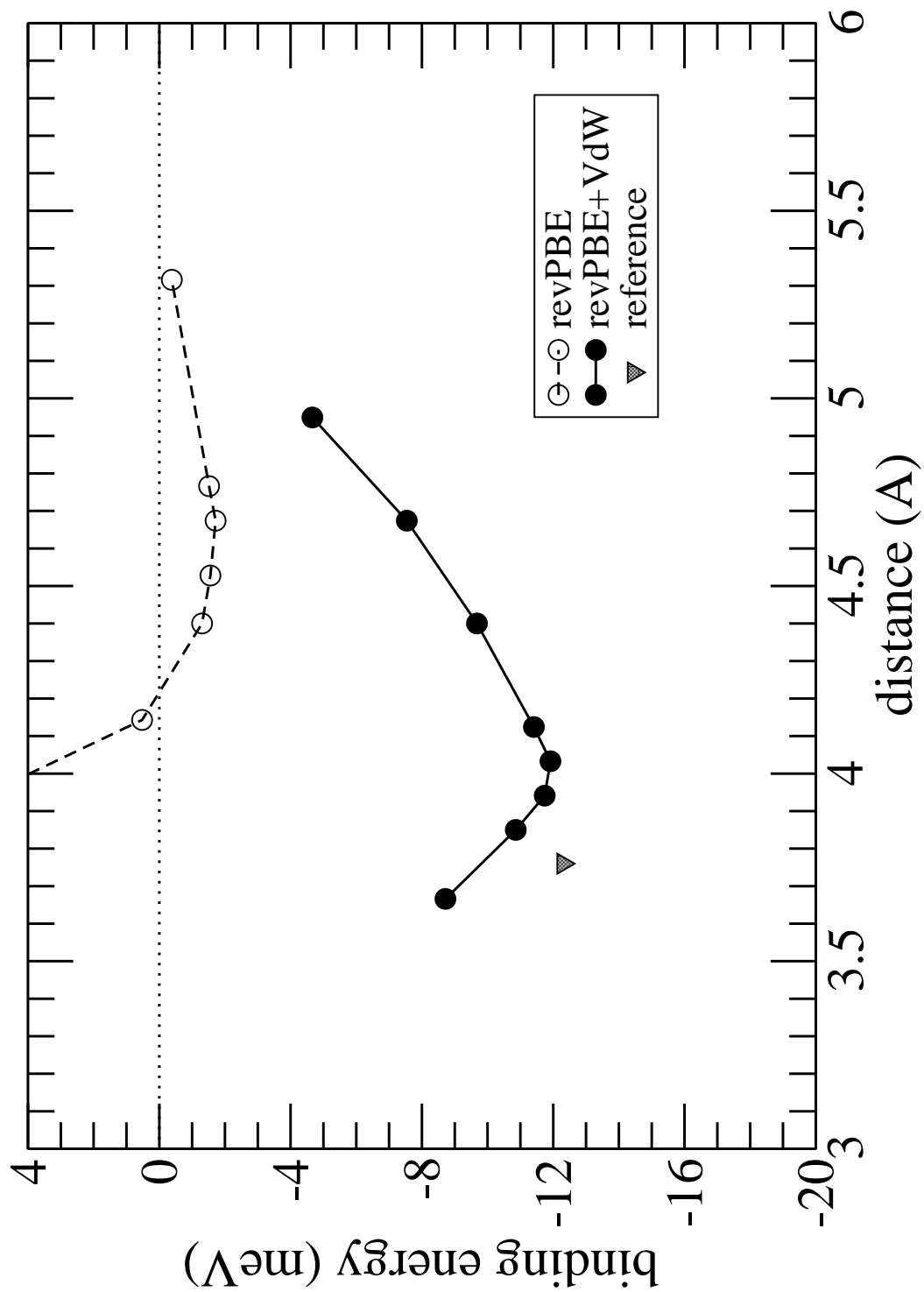


FIG. 1: Binding energy of the Ar<sub>2</sub> dimer, as a function of the Ar-Ar distance, using the standard DFT-revPBE calculation and including the VdW correction.